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C. P. Sasso
*IEN Galileo Ferraris*

M. Pasquale
*IEN Galileo Ferraris*

L. Giudici
*IEN Galileo Ferraris*

S. Besseghini
*Istituto per l'Energetica e le Interfasi*

E. Villa
*Istituto per l'Energetica e le Interfasi*

***See next page for additional authors***

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# Magnetostructural transitions and adiabatic temperature variation in polycrystal and single-crystal $Ni_2MnGa$ alloys

C. P. Sasso,[a] M. Pasquale, and L. Giudici
*IEN Galileo Ferraris, Strada delle Cacce 91, I-10135, Torino, Italy*

S. Besseghini and E. Villa
*CNR-IENI, C.so Promessi Sposi 29, I-29300, Lecco, Italy*

L. H. Lewis
*Materials Department, Brookhaven National Laboratory, Upton, New York 11973-5000*

T. A. Lograsso and D L. Schlagel
*Metals Development, Ames Laboratory, Ames, Iowa 50011*

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The magnetocaloric response of off-stoichiometric $Ni_2MnGa$ polycrystal and single-crystal samples with a Curie temperature coincident with the martensitic transition temperature was investigated. The direct measurement of temperature change ($\Delta T_{ad}$) during an adiabatic transformation under a maximum field variation $\Delta H = 5.6 \times 10^6$ A/m (7 T) was performed. The polycrystalline sample shows a maximum $\Delta T_{ad} \approx 1.5$ K at a temperature close to the structural transition. The value of $\Delta T_{ad}$ and the 20 K span of the $\Delta T_{ad}$ peak encourage further studies of the effect of microstructure on the magnetocaloric response of $Ni_2MnGa$. © *2006 American Institute of Physics*.
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## I. INTRODUCTION

Solid state cooling using the magnetocaloric effect (MCE) is an attractive novel technology which promises efficient refrigeration with a lower environmental impact. A particularly large MCE has been observed in ferromagnetic materials presenting a first-order magnetostructural phase transition such as in $Gd_5(Si_{1-x}Ge_x)_4$, $MnFeP_{0.45}As_{0.55}$, La(FeSi), and $Ni_2MnGa$.[1–6,10,11] In adiabatic conditions the transitions are accompanied by large temperature changes up to 8–10 K under a field change $\Delta H$ of the order of 5 T.

In this paper the magnetocaloric response of a polycrystalline $Ni_2MnGa$ sample having a coincident magnetostructural transition was investigated. Analogies and differences are discussed with reference to the single-crystal case in order to establish how the magnetocaloric effect is influenced by the crystalline structure and whether a cheaper polycrystalline alternative can compete with a single crystal in terms of its adiabatic temperature change. A notable adiabatic temperature change of 0.45 K at 1 T ($8 \times 10^5$ A/m) and 1.5 K at 7 T ($5.6 \times 10^6$ A/m) was measured with a polycrystal, to be compared with 0.53 K at 1 T and 3 K at 7 T in the single-crystal (SC) case.

The $Ni_2MnGa$ Heusler alloy is a shape memory material which undergoes a martensitic phase transformation when cooled below the temperature $M_f$ starting from the high temperature austenite, which is stable at $T > A_f$. Three temperatures define the start ($M_s$ and $A_s$), peak ($T_M, T_A$) and finish ($M_f$ and $A_f$) of the direct and inverse first-order phase transitions, respectively. $T_c$ is the Curie point.

An off-stoichiometric $Ni_2MnGa$ polycrystalline sample was selected with coincident transition and Curie temperature $T_A \approx T_C$. When heated from the martensitic state the samples transforms from the ferromagnetic-martensitic phase to the paramagnetic-austenitic one. The inverse transition occurs during cooling from the austenitic phase. The magnetization versus temperature curve at constant applied magnetic field $M(T)_H$ presents a discontinuous behavior and a large slope around the phase transition temperatures $T_A$ and $T_M$, (see Fig. 2). According to the Maxwell relation

$$\left(\frac{\partial S(T,H)}{\partial H}\right)_T = \left(\frac{\partial M(T,H)}{\partial T}\right)_H, \tag{1}$$

connecting the entropy and magnetic quantities within a system at thermodynamic equilibrium, the larger the slope of the $M(T)_H$ curve is, the larger the entropy change induced by a given magnetic field will be. Integrating the Maxwell relation, Eq. (1), the entropy change during isothermal transformations can be estimated from a set of hysteresis loops carried out at different temperatures near $T_A$. In Ref. 7 a large entropy change in a $Ni_2MnGa$ polycrystalline sample with $T_A \approx T_C$ was determined.

In the polycrystalline sample that we analyzed, an isothermal entropy change $|\Delta S|_{poly} \approx 1-2$ J/kg K at $\Delta H = 800$ kA/m (1 T) was determined. This value should be compared with $|\Delta S|_{SC} \approx 18$ J/kg K for an oriented SC under the same field variation. Due to the influence of the heat capacity at the transition in the presence of intense fields, the maximum adiabatic temperature variation $\Delta T$ in the polycrystal is $\Delta T_{ad} \approx 1.5$ K at $\Delta H = 5.6 \times 10^6$ A/m (7 T), half of the corresponding value for the SC, $\Delta T_{ad} \approx 3$ K. As already pointed out and discussed in Refs. 6 and 9 the entropy is not a reliable parameter to quantify the magnetocaloric response in transition metal alloys, since the specific heat of the substance plays a crucial role in determining the MCE.

[a]Electronic mail: sasso@ien.it

 

TABLE I. Martensite-to-austenite ($A_s$-$T_A$-$A_f$) and austenite-to-martensite ($M_s$-$T_M$-$M_f$) phase transition temperatures for the two polycrystal (PC) and single-crystal (SC) samples.

| Sample | $A_s$ | $T_A$ | $A_f$ | $M_s$ | $T_M$ | $M_f$ |
|---|---|---|---|---|---|---|
| $Ni_{55}Mn_{20}Ga_{25}$ SC | 306 K | 314 K | 320 K | 305 K | 300 K | 294 K |
| $Ni_{47}Mn_{33}Ga_{20}$ PC | 354 K | 360 K | 365 K | 348 K | 343 K | 334 K |

## II. EXPERIMENT AND ANALYSIS

A polycrystalline $Ni_{47}Mn_{33}Ga_{20}$ alloy was prepared by arc melting high purity elements and annealing at 800 °C for 5 h in an Ar atmosphere to homogenize its structure. A $10 \times 3 \times 3$ mm$^3$ rectangular sample was cut. A single crystal of composition $Ni_{55}Mn_{20}Ga_{25}$ was also prepared by a similar procedure to obtain the as-cast ingot which was then followed by growth in a resistance furnace in an alumina Bridgman style crucible, withdrawing the sample from the heat zone at a rate of 5 mm/h. The as-grown crystal was oriented in the austenite phase to the appropriate crystallographic direction using back-reflection Laue and a 3 mm edge cube was cut with {100} faces.

In order to determine the phase transition temperatures ($A_s$-$T_A$-$A_f$ and $M_s$-$T_M$-$M_f$) both samples were subjected to DSC analysis at a rate of 5–10 K/min in Ar flux. Table I reports the phase transition temperatures (see also Fig. 1).

The temperature dependence of magnetization at constant bias field $[M(T)_H]$ and the isothermal magnetization curves $[M(H)_T]$ were measured by Vibrating Sample Magnetometry (VSM) for the polycrystalline sample and by a SQUID magnetometer for the single-crystal sample (see Figs. 2 and 3).

$M(T)_{H_a}$ curves are presented in Fig. 2. All the $M(T)_{H_a}$ curves show a discontinuity in proximity of the phase transition temperatures (much more pronounced in the single-crystal case).

The magnetization curves $M(H)$ of Fig. 3 present two different characters associated either with the ferromagnetic or paramagnetic behavior and this notable change in saturation magnetization for small temperature variations is associated with particularly large $\Delta S$ values.

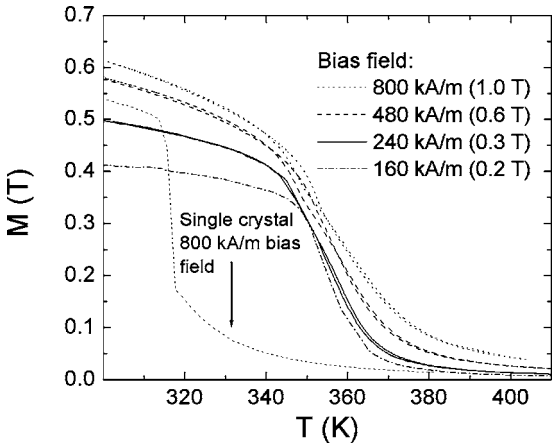


FIG. 2. Magnetization vs temperature at different bias magnetic fields $H_a$ $[M(T)_{H_a}]$ measured on the $Ni_{47}Mn_{33}Ga_{20}$ polycrystalline sample. Dotted line: $M(T)_H$ curve measured on the $Ni_{55}Mn_{20}Ga_{25}$ single crystal during heating.

In order to directly measure the temperature change associated with a large magnetic field variation an adiabatic cell was built. The sample temperature and the lattice entropy change according to the adiabatic requirement that the total entropy of the body must be conserved during the transformation. Using a superconducting coil, a field up to $5.6 \times 10^6$ A/m (7 T) was applied and varied at a rate of (1 T min$^{-1}$). A very precise temperature control, with a drift $<0.01$ K/min, was achieved using an adiabatic shield controlled by proportional-integral-differential (PID) logic. The temperature of the sample was measured by direct contact with a copper-constantan thermocouple.

It was recently shown[6] that due to the role of $C_p$ in transition metal alloys, MCE characterization is better achieved using $\Delta T$ rather than $\Delta S$ values. Using the latent heat determined from the peaks of the DSC curves of Fig. 1 we measure the entropy change in zero field

$$\Delta L = \int_{A_s}^{A_f} \frac{dQ}{dT} dT; \quad \Delta S = \int_{A_s}^{A_f} \frac{dQ}{TdT} dT. \tag{2}$$

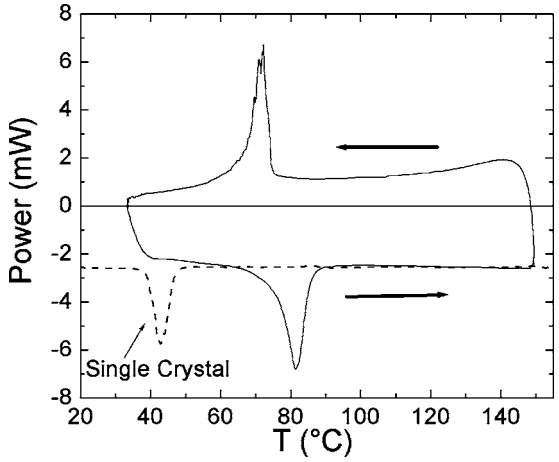


FIG. 1. Differential scanning calorimeter curves. Bottom curves: endothermal heating. Top curves: exothermic cooling. Solid line: $Ni_{47}Mn_{33}Ga_{20}$ polycrystalline sample. Dashed line: $Ni_{55}Mn_{20}Ga_{25}$ single crystal.

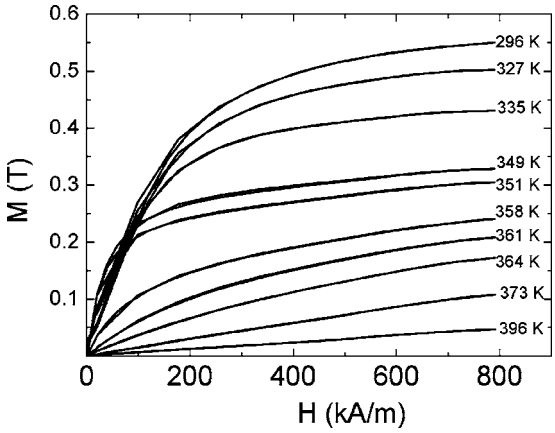


FIG. 3. Isothermal magnetization curves $[M(H)_T]$ measured on the $Ni_{47}Mn_{33}Ga_{20}$ polycrystalline sample. Paramagnetic ($T > 358$ K) and ferromagnetic ($T < 358$ K) behavior are observed.

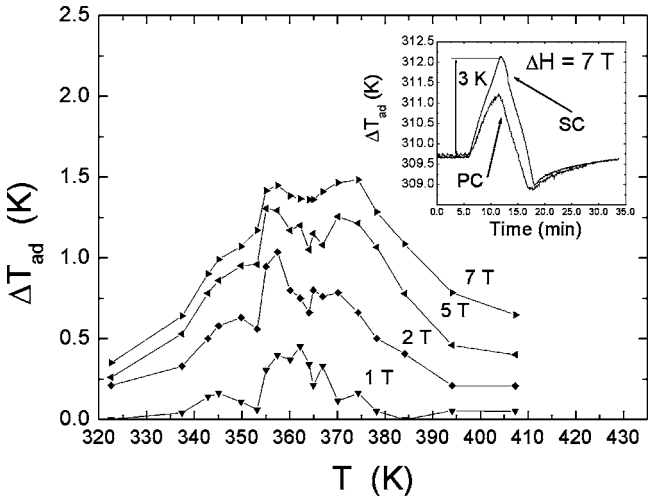


FIG. 4. Maximum adiabatic temperature change corresponding to a magnetic field variation from zero to $\Delta H=1$ T, 2 T, 5 T, 7 T plotted vs temperature $[\Delta T_{ad}(T;\Delta H)]$. A 20 K wide plateau is observed for $\Delta H=7$ T. Inset: example of $\Delta T_{ad}(\Delta H)_T$ data obtained in the polycrystal and single crystal; $\Delta H=7$ T at a rate of 1 T/min.

Due to the wider peak shown in Fig. 1, the latent heat of the polycrystalline sample, $\Delta L_{poly}$, is much larger than $\Delta L_{SC}$ in the single-crystal case: $\Delta L_{poly}=21$ kJ/kg while $\Delta L_{SC}=7$ kJ/kg, with corresponding entropy changes $|\Delta S_{poly}|=58$ J kg$^{-1}$ K$^{-1}$ and $|\Delta S_{SC}|=24$ J kg$^{-1}$ K$^{-1}$, where the difference is mainly due to the different transition temperatures $T_A$ in the two cases.

When the transition occurs under a magnetic field, the entropy change increases and very different values of $\Delta S$ can be obtained both in the single-crystal and the polycrystal case using the Maxwell approach.[6,7] Entropy change versus temperature $\Delta S(T)_{\Delta H}$ for a magnetic field varying from zero to $H$ ($\Delta H=H$) was determined by integrating Eq. (1) between the proper limits.

In the polycrystalline sample, the maximum isothermal entropy change deduced from the data of Fig. 3 is $|\Delta S|_{\Delta H=1\ T}\approx 1.3$ J/kg K. This is a rather small value when compared to the single-crystal value, where the same field variation leads to $|\Delta S|_{\Delta H=1\ T}\approx 18$ J/kg K, but it is in good agreement with the value reported in Ref. 7 for one of the polycrystalline samples under similar conditions. This smaller $\Delta S$ change is compatible with the less pronounced discontinuity of the $M(T)_H$ curves at $T_A$ observed in the polycrystal with respect to the SC case or another polycrystal sample also investigated in Ref. 7. It is expected that a more ordered and regular crystalline structure will produce an enhanced MCE. Much larger values of $\Delta S$ (up to 86 J/kg K) can be obtained at a large field, above $4.0\times 10^6$ A/m (5 T), if at least a partial phase transition is induced by the field. This behavior, typical of MCE materials has also been observed in $Ni_2MnGa$ polycrystals[7] and single crystals.[1,6,8]

Unfortunately such large $\Delta S$ values do not correspond to equivalently large $\Delta T_{ad}$ values. A summary of the $\Delta T_{ad}$ results corresponding to different $\Delta H$ values for the polycrystalline sample is reported in Fig. 4. Data were collected during a cooling run, from a temperature well above $A_f$ (400 K), using the procedure described in Ref. 6. In the inset of Fig. 4 the typical temperature response of the polycrystal for a field variation $\Delta H=5.6\times 10^6$ A/m (7 T) is compared to that of the single crystal. One can note that the temperature variation is proportional to the applied field. As expected, the temperature increases when magnetic field is increased and decreases when the magnetic field is removed. The maximum $\Delta T_{ad}$ observed in the single crystal for a field variation $\Delta H=5.6\times 10^6$ A/m (7 T) is twice that of the polycrystalline sample.

The entropy change estimated from the magnetization curves of Fig. 2, $|\Delta S|=1.3$ J kg/K, yields a corresponding adiabatic temperature change $\Delta T_{ad}\approx 0.45$ K for a field variation $\Delta H=8\times 10^5$ A/m (1 T) (see Fig. 4). However the increase of $\Delta T_{ad}$ with field is not linear, and for a larger $\Delta H=5.6\times 10^6$ A/m (7 T) the adiabatic temperature change reaches a saturation value of $\Delta T_{ad}\approx 1.5$ K. The differences in the MCE response between the polycrystalline and the single-crystal sample can be partially explained by the larger latent heat of the phase transition $\Delta L_{poly}=21$ kJ/kg while $\Delta L_{single}=7$ kJ/kg: a much larger energy is then required to transform the martensite phase into the austenite phase and such a large contribution can hardly be provided by an applied magnetic field. Another aspect is the peak of the $\Delta T_{ad}(T;\Delta H)$ curves (Fig. 4) which is rather broad around the temperature $T_M$ and this feature may be useful to achieve a wide MCE interval: for $\Delta H=5.6\times 10^6$ A/m (7 T) a 20 K wide plateau is observed with $\Delta T_{ad}(T)\approx 1.5$ K. This widening of the $\Delta T_{ad}(T)$ curves may be associated with the long magnetization tail above $T_C$ in the $M(T)_H$ curves (see Fig. 2), which becomes larger with increasing bias fields (see Fig. 2 and Ref. 6 for the single crystal). This tail is connected to the stabilization of the residual ferromagnetic-martensite phase by the applied magnetic field above $A_f$. In spite of a less pronounced magnetocaloric response with respect to single crystals or other rare-earth based alloys, polycrystalline NiMnGa samples show interesting adiabatic temperature changes which encourage further investigations.

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